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# Effect of Crystalline Structure and Impurity Content of $C_{60}$ Thin Films on the Order/Disorder Phase Transition

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## ABSRACT

Near the temperature of 260 K, $C_{60}$ crystal is known to undergo a first order phase transition, associated with changes in molecular rotations. The present paper reports the effect of the crystalline structure and impurity content of $C_{60}$ thin films on their structural behavior near this phase transition. Polycrystalline $C_{60}$ films with different grain sizes and oxygen content were obtained by varying the conditions of their vacuum deposition and post-grown exposure. Temperature-resolved X-ray diffraction in the range 300 - 15 K was used to determine the lattice parameter and its changes near the phase transition temperature. Decrease in grain sizes and increase in oxygen content of the films are found to lead to a gradual reduction in the discontinuity in lattice parameter and the transition temperature.

## INTRODUCTION

Solid $C_{60}$ is a molecular crystal with $C_{60}$ molecules occupying the lattice sites of a face-centered cubic (*fcc*) structure at room temperature [1]. $C_{60}$ molecules have a rotational degree of freedom in the crystal. The $C_{60}$ crystal is known to undergo a phase transitions associated with changes in the molecular rotations. Near the temperature $T_c$ = 260 K, $C_{60}$ crystal undergoes a first order phase transition from the *fcc* structure above $T_c$ to a simple cubic (*sc*) structure below $T_c$ [2-4]. $C_{60}$ molecules have been found to rotate freely in the *fcc* phase while rotation locks into specific orientations in the *sc* phase.

However, the published data dealing with this phase transition in $C_{60}$ thin films are very contradictory because of the fact that the films grown under different deposition conditions and/or subjected to different post-growth exposures may have substantially various crystalline structure and impurity content. On the other hand, no systematic study of the effect of the crystalline structure and impurity content of $C_{60}$ films on their behavior near the phase transition have been performed. This paper reports the first results of such kind of study.

## EXPERIMENTAL DETAILS

$C_{60}$ thin film was deposited by a vacuum deposition technique on substrates of mica, optical glass and optical glass predeposited with an Ag sub-layer. The starting $C_{60}$ powder ('Super Gold

Grade', > 99.9%) was commercially obtained from Hoechst AG. Detailed description of the deposition conditions was given elsewhere [5-8].

The thickness of all $C_{60}$ films under the present study was about 100 nm.

The crystalline structure of the $C_{60}$ films was characterized by X-ray diffraction (XRD) in Cu- and Fe-$K_\alpha$ radiation, at room temperature, and then was studied by temperature-resolved XRD in the temperature range from 300 K to 15 K, using a home-made liquid-helium cryostat. The XRD patterns also included reflections from a reference substance (high-purity Cu). Use of this modified reference XRD technique made it possible to reduce the error in our determination of the lattice parameter, which is particularly important when studying its temperature dependencies. The error in determining the lattice parameters did not exceed $\pm$ 0.02%. The sample temperature was measured with a platinum resistance thermometer.

The morphology of the front surface of the film was studied by the Atomic Force Microscopy (AFM).

## RESULTS AND DISCUSSION

The film deposited at a rate of 0.2-0.4 Å/s on a glass substrate, held at 443 K (sample 1 in table I) was found to consist of two phases: amorphous and polycrystalline with grain sizes of 20 - 50 nm. The latter was characterized by the Bragg reflections (111), (220) and (311) of *fcc* $C_{60}$ lattice with approximately the same intensities. The room-temperature XRD pattern of such a film is similar to one displayed in Fig. 2c in Ref. 5.

**Table I.** Growth conditions, structural characteristics and parameters of the *fcc/sc* phase transition for our $C_{60}$ thin films together with the published data [2-4] for $C_{60}$ single crystals.

| Sample | Substrate material | Substrate temperature (K) | Depositon rate (Å/s) | Crystalline structure of the $C_{60}$ films | Grain size in the film surface (nm) | $T_c$ (K) | $\Delta a/a$ (%) |
|---|---|---|---|---|---|---|---|
| 1 | glass | 443 | 0.2-0.4 | amorphous/ polycrystalline | 10 - 20 | - | - |
| 2 | Ag/glass | 473 | 18-20 | <111> textured polycrystalline | 100 - 200 | 250 | 0.06 |
| 3 | mica | 473 | 15 | <111> textured polycrystalline | 500 - 1500 | 252 | 0.22 |
| $C_{60}$ single crystals | - | - | - | - | - | 260 | 0.31-0.33 |

Our approach for the deposition of well-ordered $C_{60}$ films [6] requires a combination of high values of $C_{60}$ deposition rate and substrate temperature (near to the temperature of equilibrium "adsorption (deposition) $\leftrightarrow$ desorption" for $C_{60}$ molecules) as well as use of a substrate with

weak surface bonding. For example, sample 2, evaporated at a rate of 18-20 Å/s onto the Ag/glass substrate at 473 K, was found to have high degree of crystallinity and strong <111>-texture. The room-temperature XRD pattern of this sample is the same as that shown in Fig. 2a in Ref. 7 and consists only of a very narrow and intensive (111) peak and its higher harmonics (222) and (333). The sizes of crystalline domains for sample 2 are relatively large. AFM measurements revealed grain sizes in the sample surface of about 200 nm.

A mica substrate also satisfies the above mentioned requirement of weak surface bonding because it is a layered material with weak van der Waals interaction between layers. We succeeded in growing $C_{60}$ thin films on a mica substrate, with crystalline structure even better than that for the films deposited on a metal sub-layer [8]. Sample 3 deposited at a rate of 15 Å/s onto a mica substrate, held at 473 K also had strong <111>-texture. However, the intensities of the peaks in its room-temperature XRD pattern (Fig. 1 in Ref. 8) were found to be substantially higher than those we observed for sample 2. The sizes of crystalline domains are also much larger. AFM revealed grain sizes in the sample surface of 500-1500 nm.

Analysis of the XRD patterns for all polycrystalline $C_{60}$ films studied points to the fact that the material at room temperature has *fcc* structure. Our room-temperature value of the lattice parameter $a$ = 14.144 Å is in good agreement with the data published for $C_{60}$ single crystals and powder bulk samples [3-4].

Figures 1 - 3 show the results of temperature-resolved XRD measurements of the lattice parameter for as-grown samples 1, 2 and 3. There is no indication of a first order phase transition for sample 1 (figure 1): only a strong but gradual decrease in the lattice parameter is observed during cooling of the sample in the temperature range from $T_{c2}$ = 250 K to $T_{c1}$ = 230 K. On the other hand, for sample 2, figure 2 demonstrates a well defined discontinuity in the lattice parameter, $\Delta a/a$ = 0.06 %, near the temperature $T_c$ = 250 K which corresponds to the *fcc/sc* phase transition [2]. For sample 3, one can also observed the first order phase transition with even higher values of $\Delta a/a$ = 0.22 % and $T_c$ = 252 K (figure 3 and table I).

Temperature dependence of the lattice parameter for sample 3 reveals two other distinct anomalies, at $T_o \approx 155$ K and $T_g \approx 95$ K, which may associate with the beginning and completion of the freezing of molecular rotation (formation of the orientational glass). These features together with their relationships with the structural characteristics of the films will be discussed elsewhere.

It should be noted that the observed values of $\Delta a/a$ and $T_c$ for our thin films are lower than those published for $C_{60}$ bulk samples (table I). Furthermore, we have demonstrated a gradual reduction in the $\Delta a/a$ and $T_c$ values with decrease of grain sizes in the $C_{60}$ films. For sample 3, with worst structural characteristics, we observed a broadening of the phase transition temperature range (phase transition of a second degree). This may be due to a relatively high density of crystalline defects (including grain boundaries), strains and impurities in $C_{60}$ thin films (in comparison with single crystals) and/or the presence of anisotropic crystallites with oriented grain boundaries. The latter originate from the strong texture of our films. Defects of crystalline structure of solid $C_{60}$ [9], impurities [9-11], strains [12], or an increased surface/volume ratio [13-14] have been demonstrated to result in a reduction of $T_c$ up to 25 K. The first two factors are known to lead also to a broadening of the phase transition temperature range (phase transition of a second degree) or even to suppress the phase transition [10,14].

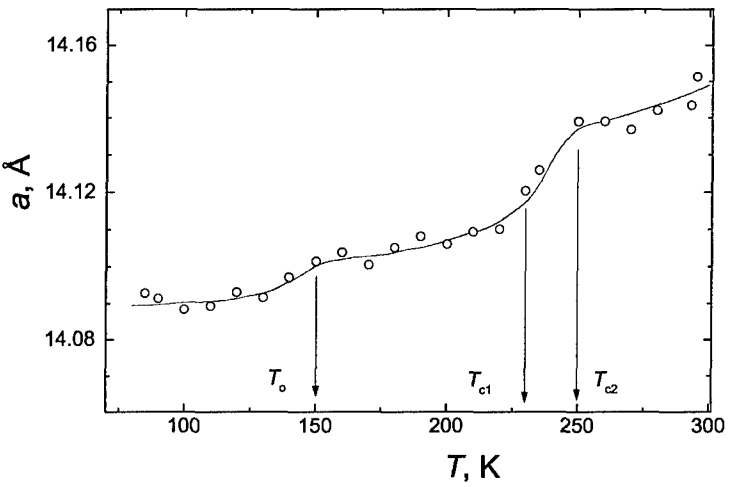


**Figure 1**. Results of XRD measurements of the lattice parameter for sample 1.

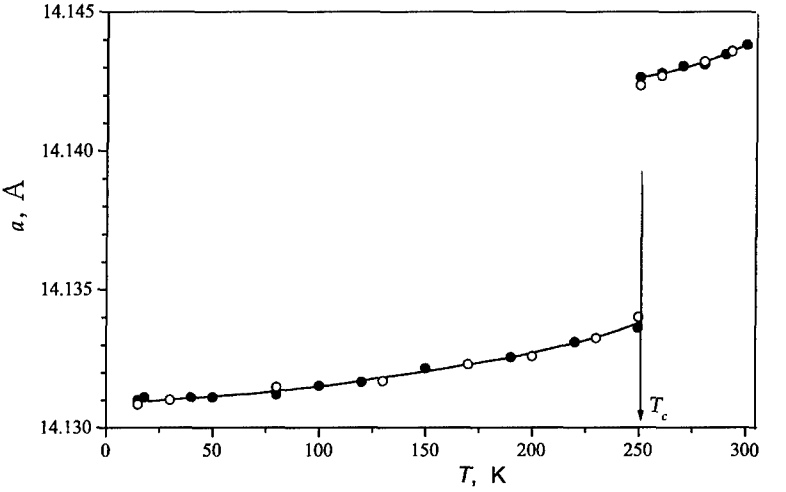


**Figure 2**. Results of two sets of XRD measurements of the lattice parameter for sample 2.

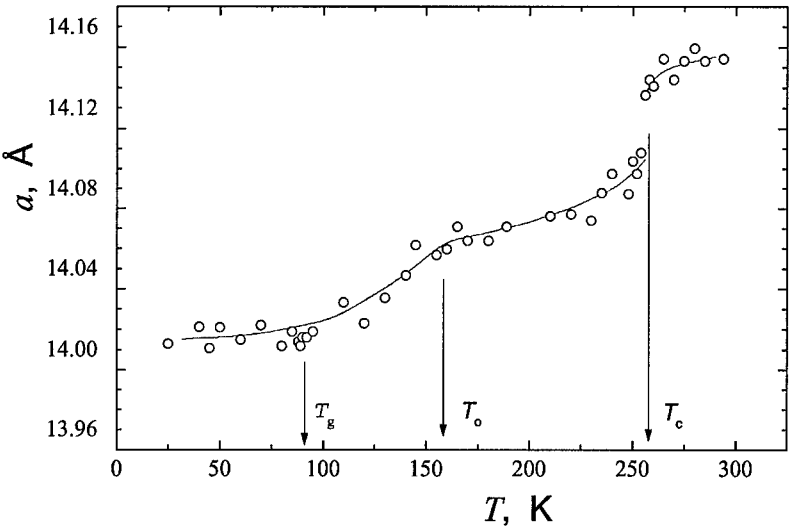


**Figure 3**. Results of XRD measurements of the lattice parameter for sample 3.

Given the large size of the interstitial sites in the $C_{60}$ crystal (the corresponding voids are more than 4 Å in diameter) molecular oxygen from air is known to diffuse readily into this solid even at room temperature [15]. We revealed that post-grown exposure of our films to air leads to an increase in their oxygen content [16] and, in turn, to reduction in the $\Delta a/a$ and $T_c$ values. Exposure of the $C_{60}$ films to air during 10 months was found to suppress any first order and even second order phase transition in the samples [17]. However, annealing of the samples at 150°C in vacuum for 2 hours may restore the as-grown structural characteristics of the films and the phase transition parameters. We explain this effect by an effusion of oxygen during the annealing.

## CONCLUSIONS

A systematic study of the effect of crystalline structure and impurity content in $C_{60}$ films on their behavior near the *fcc/sc* disorder/order phase transition have been performed by the temperature-resolved X-ray diffraction measurements. Decrease of grain sizes in the films was found to result in a gradual reduction in the discontinuity in lattice parameter and the transition temperature. Increase in impurity (oxygen) content in the films led to the same result and even suppressed the phase transition.

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